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Approaches Towards the Synthesis of a  
2,9,16,23-tetrasubstitutedphthalocyanine as a Pure Isomer

By

Shafrira Greenberg, A.B.P. Lever and Clifford C. Leznoff\*

in

Canadian Journal of Chemistry

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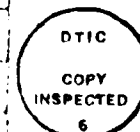
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Approaches Towards the Synthesis of a  
2,9,16,23-tetrasubstitutedphthalocyanine as  
a Pure Isomer

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# ABSTRACT

Treatment of 4-neopentoxyphtalonitrile with hydrogen sulfide gas yielded 1-imino-6-neopentoxy-3-thioisoindoline and 1-imino-5-neopentoxy-3-thioisoindoline, which on alkylation with iodomethane gave 1-imino-3-methylthio-6-neopentoxyisoindolenine and 1-imino-3-methylthio-5-neopentoxyisoindolenine. The methylthioisoindolenines readily condensed at room temperature to a mixture of tetrasubstituted phthalocyanines and a series of linear open-chained purple compounds characteristic of isoindigos, while condensation at  $-20^{\circ}\text{C}$  in the presence of zinc acetate gave, in at least one experiment, 2,9,16,23-tetraneopentoxy phthalocyanine as a pure isomer. The low temperature formation of phthalocyanines is remarkable and the syntheses described herein provide guidelines for the synthesis of pure isomers of 2,9,16,23-tetrasubstitutedphthalocyanines. The purple and red compounds are shown to have isoindigo structures rather than a ring opened phthalocyanine structure as previously reported.

Tetrasubstituted phthalocyanines having one substituent on each of the four benzo rings of phthalocyanines have been known for some time (1) but have received more attention recently due to their importance in electrocatalytic studies (2,3). Most tetrasubstituted phthalocyanines are prepared by self-condensation of a suitable 3 or 4-substituted phthalonitrile or derivative (4,5). For example the isoindoline of 4-neopentoxypthalonitrile will, upon condensation, give not only 2,9,16,23-tetraneopentoxypthalocyanine (1) but also the 2,10,16,24-2,9,17,24-, and 2,9,16,24-tetraneopentoxypthalocyanines isomers (6,7). Indeed, we have shown that 2,9,16,23-tetraneopentoxypthalocyanine zinc (II) (2) derivative exhibited peaks in its  $^1\text{H}$  nmr spectrum exhibiting the presence of seven of the possible eight environments collectively present in the four isomers (7). A full discussion of this phenomenon was also recently demonstrated for some quaternized tetra-2,3-pyridinoporphyrazines (8). In this latter example, it was suggested, that steric considerations favoured the symmetrical isomer, having  $\text{C}_{4h}$  symmetry, but that the other isomers were present in lesser amounts. Virtually all tetrasubstituted phthalocyanines known in the literature (1) exist as a mixture of the four possible isomers and in the case of substituents at the 2 position are usually referred to as the 2,9,16,23-tetrasubstituted isomer. In some instances authors, have simply selected one of the other isomers as the indexed name but again this did not imply exclusive formation of that particular isomer (9).

In connection with our studies on multinuclear phthalocyanine (6,7,10) and the possibility of obtaining one pure isomer of a binuclear phthalocyanine for X-ray diffraction studies we were interested in exploring synthetic methods of phthalocyanine formation that could give rise exclusively to 2,9,16,23-tetrasubstituted phthalocyanines as one isomer. In a previous paper we had shown that dithioamides do form phthalocyanines with diiminoisoindolines at modest temperatures (11). We envisioned that a 5-substituted iminothioamide

should self-condense in one direction to form exclusively a 2,9,16,23-tetrasubstituted phthalocyanine as one isomer, as the imino group on one side of the molecule should displace selectively the methylthio group on the other side of a second molecule. It turns out that treatment of phthalonitrile (3) with hydrogen sulfide gas gives 1-imino-3-isoindoline (4) directly as reported by Baguley and Elvidge (12), but 4 does not readily condense to phthalocyanine under normal conditions (4,5). Despite the fact that we were unable to successfully S-alkylate dithioamides (11) under a variety of conditions, we found that the iminothioamide 4 is readily alkylated to a separable mixture of N-methyl-2,3-dihydro-3-thioxo-1H-isoindol-1-one (5) and 1-imino-3-methylthioisoindolenine (6). The S-alkyl derivative 6 readily condenses to phthalocyanine (7) under the usual conditions but at room temperature instead of 150°C (Scheme I).

#### Scheme I

This encouraging result led us to examine the possibility of using a substituted 1-imino-3-methylthioisoindolenine in the exclusive formation of 2,9,16,23-tetrasubstituted phthalocyanines as one isomer. Treatment of 4-neopentoxypthalonitrile (8) with hydrogen sulfide (12) gave a mixture of 1-imino-6-neopentoxy-3-thioisoindoline (9) and 1-imino-5-neopentoxy-3-thioisoindoline (10), separable by flash chromatography (13). In separate experiments pure 9 and 10 were treated with iodomethane to give 1-imino-3-methylthio-6-neopentoxyisoindolenine (11) and 1-imino-3-methylthio-5-neopentoxyisoindolenine (12) respectively. In separate experiments, compounds 11 and 12 self-condensed spontaneously at room temperature to 2,9,16,23-tetraneopentoxypthalocyanine, as a mixture of isomers as analyzed previously by <sup>1</sup>H nmr spectroscopy (7). In addition a mixture of

purple coloured compounds (13-16) could be recovered by flash chromatography. The assignments of the structures of compounds 13 to 16 remain tentative and are based on mass spectroscopy, high resolution mass spectroscopy, nmr, and uv/vis spectroscopy. Mass spectroscopy of this mixture of purple compounds could be accounted for by a mixture of compounds (13-16) exhibiting parent ions for all of the compounds. Further purification gave small quantities of pure 13 and 14 whose structures are consistent with their exact high resolution mass spectra. Interestingly, the  $^1\text{H}$  nmr of 13 and 14 were consistent with the assigned structures but the absorptions for the neopentoxy substituents indicated that 13 and 14 were formed as one isomer each and that mixtures of isomers in which the position of the neopentoxy groups was different in each benzo ring were not obtained. Alternatively, the absorptions of the different positional isomers of 13 and 14 could have been coincident but this possibility is unlikely.

#### Scheme II

We were interested in characterizing the precursors 4-6 and 9-11 by  $^{13}\text{C}$  nmr spectroscopy but found that it was necessary to obtain  $^{13}\text{C}$  nmr spectra of pure 1,3-diimino-5-neopentoxyisoindoline (17) (see experimental) and monoiminophthalimide (18) (14) (Figure 1). Using the  $^{13}\text{C}$  nmr of 17 and 18 it was possible to assign the absorptions of 4-6 and 9-11 (Table 1). In addition the uv spectra of 4-6, 9-11 and 17 are recorded in Table 2.

Fig. 1

Table 1

Table 2

It is well known that aromatic thioamide undergo condensation to isoindigo dyes (12), so that the formation of 13 to 16 is not too surprising. The presence of the neopentoxy substituents of 13-16 solubilized these normally poorly soluble compounds and allowed us to effect a separation to isolate pure 13 and 14. The uv/vis spectra of 13 and 14 are very unique and neither resembles phthalocyanines nor isoindigos. In a recent paper Fujiki et al (15) describe the preparation of a hydroxygermanium (IV)  $\alpha,\beta,\gamma$ -triazabenzcorrole formed by a ring contraction of dichlorogermanium phthalocyanine. Light illumination of this corrole derivative is reported (15) to give a red compound whose uv/vis is identical to 13 and 14. These authors propose three structures 19-21 for their red compound, none of which would be consistent with the carbon-carbon double bond structure of 13 and 14. In light of our results a possible structure for their red compound could be illustrated below.

Fig. 2

A representation of their red compound by the structure 22 in Fig. 2 would be likely and would not involve cleavage of a carbon-carbon double bond. Repetition of the work by Fujiki et al (15) using neopentoxysubstituted phthalocyanines would give soluble derivatives of their red compound which could be purified and adequately characterized.

Condensation of 11 or 12 at  $-20^{\circ}\text{C}$  in dimethylformamide (DMF) and using  $\text{Zn}(\text{OAc})_2$  as a template for macrocycle formation gave 2 directly and a mixture of purple compounds likely 13-16. In two experiments, condensation of 11 or 12 led to 2,9,16,23-tetraneopentoxyphthalocyanine 2 as mainly one isomer when examined by  $^1\text{H}$  nmr spectroscopy (Table 3), but larger scale preparations of this reaction again led to 2 but only as a mixture of isomers. It should be pointed out that

the mixture of isomers thus obtained was not identical to the statistical distribution of isomers of 2 previously reported (7) (Table 3).

TABLE 3

In summary, we have demonstrated the remarkable low temperature formation of phthalocyanines from iminomethylthioisindolenines, have aided in the characterization of the coloured by-products formed in these as similar reactions, and have initiated experiments directed towards the isolation of pure isomers of tetrasubstituted phthalocyanines.

#### EXPERIMENTAL

Matheson high purity argon was used to maintain inert atmosphere conditions. Infrared (ir) spectra were recorded on a Pye Unicam SP1000 infrared spectrophotometer using KBr discs for solids or as neat films between NaCl discs. Nuclear magnetic resonance (nmr) spectra for carbons and protons were recorded on a Bruker AM300 nmr spectrometer using deuteriochloroform as solvent and tetramethylsilane as the internal standard unless otherwise stated. The positions of the signals are reported in  $\delta$  units. (The splittings of the signals are described as singlets (s), doublets (d), triplets (t), quartets (q), or multiplets (m).)

The visible-ultraviolet spectra (uv) were recorded on a Hewlett Packard HP8451A Diode Array spectrophotometer. Mass spectra (ms) were recorded at 70 eV on a VG Micromass 16F mass spectrometer in the EI mode.

Melting points (mp) were determined using a Kofler hot stage melting point apparatus and are uncorrected. Thin layer chromatography (tlc) was performed using silica gel G as the adsorbent. Flash chromatography was performed using silica gel of particle size 20-45 microns. All reactions were stirred with a magnetic stirrer. All solvents were freshly distilled before use. Microanalyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ont.

#### Purification of 5-neopentoxy-1,3-diiminoisoindoline (17)

The crude 5-neopentoxy-1,3-diiminoisoindoline obtained from 134 mg of 4-neopentoxyphthalonitrile (0.63 mmol) by standard procedure (6) was dissolved in ethyl acetate and washed with water and dried over anhydrous magnesium sulfate. Evaporation of the ethyl acetate and recrystallization from ethyl acetate/hexanes gave in 68% yield 98 mg of pure 5-neopentoxy-1,3-diiminoisoindoline as white crystals, mp 200-203°C; ir ( $\text{cm}^{-1}$ ): 3260 (NH), 3200 (NH), 1695, 1650, 1620-1600, 1540, 1450, 1440, 1315, 1240, 1140, 1065, 1020, 885, 820;  $^1\text{H}$  nmr  $\delta$ : 7.59 (d,  $J = 8.4$ , 1H), 7.24 (br, 1H), 7.12 (dd,  $J = 8.4$ , 2.1, 1H), 3.70 (s, 2H,  $\text{CH}_2\text{O}$ ), 1.06 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ); ms  $m/z$ : 231 ( $\text{M}^+$ , 25), 161 ( $\text{M}^+ - 70$ , 80), 71 (38), 57 (47), 43 (100). Anal. calcd. for  $\text{C}_{13}\text{H}_{17}\text{N}_3\text{O}$ : C 67.51, H 7.41, N 18.17; found: C 68.01, H 7.74, N 18.05.

#### 1-Imino-3-thioisoindoline (4)

The 1-imino-3-thioisoindoline was prepared from phthalonitrile and sodium hydrogen sulfide according to the procedure of Baguley and Elvidge (12), mp 220°C decomposed (lit. (12) mp 218°C); ir ( $\text{cm}^{-1}$ ): 3160 (NH), 1665, 1465, 1390, 1290, 1270, 1240, 1080, 910, 765, 675;  $^1\text{H}$  nmr (DMSO,  $d_6$ )  $\delta$ : 10.88 (vbr, 2H, NH), 7.99 (d,  $J = 7.3$ , 1H), 7.81 - 7.67 (m, 3H); ms  $m/z$ : 162 ( $\text{M}^+$ , 100), 146 (20), 135 (30), 129 (92), 76 (47).



1-Imino-3-methylthioisindolenine (6) and N-methylmonothiophthalimide (5)

A solution of 101 mg of 1-imino-3-thioisindoline (0.63 mmol) in 1 mL ethanol was methylated with dimethyl sulfate according to the procedure of Baguley and Elvidge (12). The crude product was precipitated from water, filtered and washed with water to give in 65% yield, 71 mg of 6. An attempt to recrystallize 6 resulted in decomposing accompanied with phthalocyanine formation, mp 86-90°C decomposed (lit. (12) mp 98-100°C); ir (cm<sup>-1</sup>): 3180 (NH), 1655, 1480, 1360, 1265, 1240, 1040, 960, 770, 760, 685; <sup>1</sup>H nmr δ: 9.49 (br, 1H), 7.93 (br, 1H), 7.55 - 7.43 (m, 3H), 2.74 (s, 3H, S-CH<sub>3</sub>); ms m/z: 176 (M<sup>+</sup>, 35), 129 (100).

When left overnight the filtrate deposited orange needles which were filtered off to give in 9% yield 10 mg of N-methylmonothiophthalimide mp 97-98°C (lit. (16) mp 97°C, 86-87°C); ir (cm<sup>-1</sup>): 1740 (C=O), 1470, 1375, 1340, 1325, 1075, 990, 770, 700; <sup>1</sup>H nmr δ: 7.96 (m, 1H), 7.77 (m, 1H), 7.69 (m, 2H), 3.48 (s, 3H, N-CH<sub>3</sub>); ms m/z: 177 (M<sup>+</sup>, 100), 117 (80).

1-Imino-6-neopentoxy-3-thioisindoline (9) and

1-imino-5-neopentoxy-3-thioisindoline (10)

A suspension of 15.1 g of sodium sulfide nonahydrate (62.9 mmol) in 5 mL of water was saturated with a slow stream of hydrogen sulfide gas for 1 h. The suspension became cloudy and the stream of H<sub>2</sub>S was increased for a further 45 min. The grey solution was then added to a solution of 4.2 g of 4-neopentoxyphthalonitrile (6) (19.6 mmol) in 11 mL of 95% ethanol and the mixture was stirred at room temperature for 48 h. The reaction mixture was diluted with 200 mL of water and the precipitate was filtered and washed with water to yield 3.9 g of crude product. Further purification was done by flash chromatography (13) on silica gel, using ether/pet ether (3:2) as eluant. The first 100 mL consisted of dark impurities and a trace of

5-neopentoxydithiophthalimide (11). Continued elution gave a yellow moving band consisting of 1-imino-6-neopentoxy-3-thioisoindoline. Evaporation of the eluant gave in 17% yield 0.84 g of pure 9 as very light brown crystals, mp 126-130°C decomposed; ir (cm<sup>-1</sup>): 3280-3180 (NH), 1660, 1610, 1490, 1480-1460, 1365, 1255, 1105, 830; <sup>1</sup>H nmr (acetone d<sub>6</sub>) δ: 7.83 (d, J = 8.4, 1H), 7.53 (br, 1H), 7.26 (dd, J = 8.4, 2.3, 1H), 3.82 (s, 2H, CH<sub>2</sub>O), 1.06 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C); ms m/z: 248 (M<sup>+</sup>, 100), 178 (82), 71 (27), 43 (28). Anal. calcd. for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>OS: C 62.87, H 6.49, N 11.28; found: C 62.95, H 6.70, N 11.42.

Continued elution of the silica gel gave a second yellow moving band consisting of 1-imino-5-neopentoxy-3-thioisoindoline. Evaporation of the eluant gave in 20% yield 0.97 g of pure 10 as golden crystals, mp 189-191°C decomposed; ir (cm<sup>-1</sup>): 3250 (NH), 1660, 1610, 1495, 1380, 1365, 1325, 1280, 1200, 1050, 1020, 865, 830, 820, 730; <sup>1</sup>H nmr (acetone d<sub>6</sub>) δ: 7.88 (d, J = 8.5, 1H), 7.37 (d, J = 2.2, 1H), 7.32 (dd, J = 8.5, 2.2, 1H), 3.83 (s, 2H, CH<sub>2</sub>O), 1.07 (s, 9H, (CH<sub>3</sub>)<sub>3</sub>C); ms m/z: 248 (M<sup>+</sup>, 42), 178 (80), 71 (52), 43 (100). Anal. calcd. for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>OS: C 62.87, H 6.49, N 11.28; found: C 63.09, H 6.75, N 11.22.

1-Imino-3-methylthio-6-neopentoxyisoindolenine (11) and

1-imino-3-methylthio-5-neopentoxyisoindolenine (12)

A solution of 64.4 mg of 1-imino-6-neopentoxy-3-thioisoindoline (0.26 mmol), 1 mL ethanol and 0.22 mL of 1.25 N sodium hydroxide (0.28 mmol) was diluted with 1 mL of water and stirred while 0.02 mL of methyl iodide (0.32 mmol) was added dropwise at room temperature. After 45 - 60 minutes ice-cold water was added and the product was filtered and washed with water to give in 82% yield 56 mg of 1-imino-3-methylthio-6-neopentoxyisoindolenine as brown crystals. Compound 11 was used directly in the next step, mp 115-117°C (turned green) ir (cm<sup>-1</sup>): 3260-3180 (NH), 1660, 1605, 1480-1460, 1360, 1250, 1100, 825; <sup>1</sup>H nmr δ: 9.34 (br, 1H), 7.46 (br, 1H), 7.35 (d, J = 8.2, 1H), 7.00 (d, J = 8.2, 1H), 3.69 (s,

2H,  $\text{CH}_2\text{O}$ ), 2.72 (s, 3H,  $\text{SCH}_3$ ) 1.05 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ) ms  $m/z$ : 262 ( $\text{M}^+$ , 10), 192 (23), 71 (65), 57 (48), 43 (100). Anal. calcd. for  $\text{C}_{14}\text{H}_{18}\text{N}_2\text{OS}$ : C 64.09, H 6.92, N 10.68; found: C 64.06, H 7.02, N 11.05.

Similarly a solution of 101 mg of 1-imino-5-neopentoxo-3-thioisindoline was methylated with methyl iodide at  $0^\circ\text{C}$  for 3 minutes to give a dark oily product. The crude product was extracted with ether and the organic layer was washed thoroughly with water. After drying over anhydrous magnesium sulfate, the solvent was evaporated to give in 75% yield 80 mg of very dark oil. Compound 12 is very unstable and therefore it is used directly in the next step. An attempt to purify 12 by flash chromatography caused decomposition, hydrolysis of the imino group, and phthalocyanine formation.  $^1\text{H}$  nmr  $\delta$ : 7.64 (d,  $J = 9$ , 1H), 7.44 (d,  $J = 3$ , 1H), 6.97 (dd,  $J = 9, 3$ , 1H), 3.73 (s, 2H,  $\text{CH}_2\text{O}$ ), 2.81 (s, 3H,  $\text{SCH}_3$ ), 1.06 (s, 9H,  $(\text{CH}_3)_3\text{C}$ ); ms  $m/z$ : 262 ( $\text{M}^+$ , 31), 247 ( $\text{M}^+ - 15$ , 9), 215 ( $\text{M}^+ - \text{SCH}_3$ , 40), 192 ( $\text{M}^+ - 70$ , 14), 145 (95), 71 (98), 43 (100).

#### Phthalocyanine formation from 11

Compound 11 obtained from 100 mg of 9 (0.40 mmol) in 1-2 mL of N,N-dimethylaminoethanol underwent self-condensation under argon at room temperature for 60 h. The crude reaction product was purified as previously described (6) to give after flash chromatography, in 5 - 18% yield, 2,9,16,23-tetraneopentoxophthalocyanine (1) as a mixture of isomers. From the  $^1\text{H}$  nmr it seemed that some isomers were more selectively formed than others, but complete selectivity was not obtained. If during the self condensation, the argon is bubbling directly inside the reaction mixture, in order to remove the ammonia which is formed during the reaction, the desired phthalocyanine is not formed at room temperature. Raising the temperature to  $60^\circ\text{C}$  (oil bath) increased the yield but reduced the selectivity of the formation of isomers. Phthalocyanine formation was observed to take place when a solution of 11 in

ether was left at room temperature overnight or when a sample of 11 was left partially dissolved in  $\text{DMSO-d}_6$  inside NMR tube. In both cases no selectivity towards the formation of one isomer was detected by  $^1\text{H}$  nmr. During the purification of 1 by flash column chromatography it was observed that some purple material was left on the top of the column. At room temperature the purple material became very intense. Therefore, after all of 1 was eluted with toluene, the solvent system was changed to 2-methoxyethanol/toluene (1:50). Several fractions were collected and after evaporation of the solvent it was found that some fractions contained only 13 and 14.  $\text{ir (cm}^{-1}\text{)}$ : 3400 (NH), 2940, 1765, 1730, 1610, 1490, 1365, 1230, 1045, 1010, 745;  $^1\text{H}$  nmr  $\delta$ : 7.75 (d,  $J = 8.3$  Hz), 7.32 (d,  $J = 2.0$  Hz), 7.20 (dd,  $J = 8.2$  and  $2.0$  Hz), 3.71 (s,  $\text{CH}_2\text{O}$ ), 1.06 (s,  $(\text{CH}_3)_3\text{C}$ ).  $^{13}\text{C}$  nmr  $\delta$ : 168.00, 167.93, 164.83, 135.24, 125.18, 124.27, 120.66, 108.57, 78.80, 31.88, 29.66, 26.44; uv (ether): 582, 542, 510, 346 nm. Further purification was achieved by preparative tlc using the same eluting solvent as above to give 13 and 14 in 5% and 7% yield respectively. ms (high resolution)  $m/z$ : calcd. for  $\text{C}_{39}\text{H}_{44}\text{N}_4\text{O}_5$ , 13, ( $\text{M}^+$ ): 648.35404; found: 648.3555. Calcd. for  $\text{C}_{52}\text{H}_{61}\text{N}_7\text{O}_5$ , 14, ( $\text{M}^+$ ): 863.47337; found: 863.4696. Compounds of related structure were discussed by Fujiki et al (15).

#### Phthalocyanine formation from 12

Compound 12 obtained from 116 mg of 10 (0.47 mmol) in 1-2 mL of  $N,N$ -dimethylaminoethanol underwent self-condensation under argon at room temperature for 18 h. The crude reaction product was purified as previously described (6) to give after flash chromatography, in 8% yield, 8 mg of 2,9,16,23-tetraneopentoxypthalocyanine as a mixture of isomers with some isomers more selectively formed than others in comparison with the isomers formed from the self-condensation of 5-neopentoxo-1,3-diiminoisoindoline (17) at  $150^\circ\text{C}$ . Further elution of the column with 2-methoxyethanol/toluene (1:50) gave

purple/red material consisting of 13 - 16 as analyzed by mass spectroscopy. The physical and spectral data of 1 (except for the  $^1\text{H}$  nmr) were identical to the ones previously reported (6).

#### 2,9,16,23-Tetraneopentoxypthalocyanine zinc (II) (2)

A mixture of 20 mg of 11 (0.076 mmol) and 5.7 mg (0.031 mmol) of zinc acetate was cooled in the freezer to  $-15^\circ\text{C}$ . Cold DMF ( $-15^\circ\text{C}$ ) was added (1 mL) and the mixture turned green and was left in the freezer for one week. The crude product was purified by flash column chromatography in a cold room ( $3^\circ\text{C}$ ). The column was packed a day in advance and was left in the cold room overnight. The crude product was applied to the column as is and was flash with cold toluene at  $3^\circ\text{C}$  to give 1 mg of 2 (5% yield).  $^1\text{H}$  nmr ( $\text{C}_6\text{D}_6$ )  $\delta$ : 1.26, 1.20; ms  $m/z$ : 922 ( $\text{M}^+$ , 100), 851 ( $\text{M}^+ - 71$ , 40), 460 ( $\text{M}^{+2} - 1$ , 65). Similarly a mixture of 12 derived from 102 mg of 10 (0.41 mmol) underwent self-condensation in the presence of zinc acetate in DMF at  $-15$  to  $-18^\circ\text{C}$ . Purification as above gave a mixture of 2 contaminated by 13 and 14. Further purification by preparative tlc using 2-methoxyethanol/toluene (1:50) as eluting solvent followed by flash column chromatography gave 10.8 mg of 2 in 11% yield.  $^1\text{H}$  nmr ( $\text{C}_6\text{D}_6$ )  $\delta$ : a major peak at 1.26 and 2 small peaks at 1.23 and 1.21 ppm. This experiment was repeated at  $-40^\circ\text{C}$  and gradually the temperature was raised to  $+5^\circ\text{C}$ . Purification as above gave a trace of the desired product.  $^1\text{H}$  nmr ( $\text{C}_6\text{D}_6$ )  $\delta$ : 1.26 ppm. A control experiment using 11 in 2-N,N-dimethylaminoethanol showed that metal free phthalocyanine formation did not take place at temperatures below  $10^\circ\text{C}$ .

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TABLE 1 -  $^{13}\text{C}$  Nuclear Magnetic Resonance Chemical Shifts in PPM( $\delta$ ) in  $\text{CDCl}_3$  of  
Some Imino and Thionalogs of Phthalimide.

Compound	Carbon										
	1	3	3a	4	5	6	7	7a	8	9	10
4 <sup>a</sup>	199.92 <sup>b</sup>	164.97 <sup>b</sup>	134.00	121.72	132.54 <sup>c</sup>	132.34 <sup>c</sup>	123.02	137.80	-	-	-
5	197.36	169.79	127.38	123.64	134.02	133.08	122.69	137.06	-	-	27.54
6	182.37	171.52	140.45	122.75	131.12 <sup>c</sup>	130.97 <sup>c</sup>	119.86	136.64	-	-	13.25
9 <sup>a</sup>	197.85	163.31 <sup>d</sup>	131.67	106.91	163.27	118.83	124.90	130.69	77.99	31.59	26.24
10 <sup>a</sup>	165.26 <sup>b</sup>	200.23 <sup>b</sup>	140.25	107.67	162.53	118.98	123.32	122.01	77.78	31.54	26.22
11	n.o. <sup>e</sup>	n.o.	n.o.	108.12	162.13	117.54	121.27	n.o.	77.83	31.58	26.24
17 <sup>a</sup>	169.17	169.17	138.80	106.89	161.56	116.70	122.21	128.51	77.76	31.60	26.30
18 <sup>a,f</sup>	172.9 <sup>b</sup>	164.5 <sup>b</sup>	134.2 <sup>b</sup>	122.0	132.9	132.3	122.5	133.1	-	-	-

<sup>a</sup> Taken in  $\text{DMSO-d}_6$ .

<sup>b</sup> Broadened.

<sup>c</sup> These values may be interchanged.

<sup>d</sup> Signal overlap with  $\text{C}_5$ .

<sup>e</sup> n.o. = not observed due to low concentration. Sample should not be heated to dissolve.

<sup>f</sup> Data taken from ref. 14.



TABLE 2 - UV Spectra of Iminothioisoindolines and Related  
Compounds in  $\text{CHCl}_3$  at  $24^\circ\text{C}$

Compound	$\lambda_{\text{max}}$ (nm) (log $\epsilon$ )
4 <sup>a</sup>	234(4.29), 310(4.13), 345(3.90)
5	242(3.75), 300(4.16), 332(4.01)
6 <sup>a</sup>	285(3.98), 436(2.72)
9	258(4.24), 340(4.23)
10	256(4.40), 326(4.28)
11 <sup>b</sup>	254(4.36), 298(4.18), 366(3.42)
17	244(4.24), 266(4.24), 312(sh) (4.12)

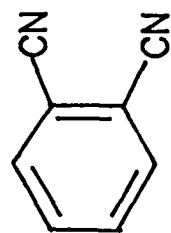
a - Data taken from ref. 12.

b - This compound is not very stable.

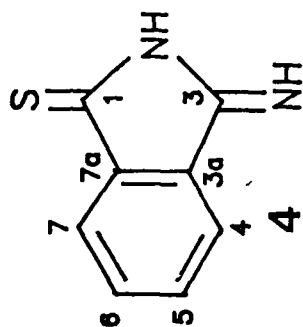
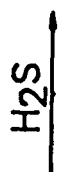
TABLE 3 -  $^1\text{H}$  Nuclear Magnetic Resonance Chemical Shift in PPM( $\delta$ ) of different Preparation of 2,9,16,23-tetraneopentoxypthalocyanine (1) and its Zn Derivative (2).

Phthalocyanine	Precursor	Reaction Conditions	$(\text{CH}_3)_3\text{C}$	NH
1	17	160°C, DMAE <sup>a</sup>	1.27, 1.26, 1.25, 1.232, 1.226	-4.94, -5.12, -5.21, -5.64
1	11	60°C, DMAE	1.29, 1.26, 1.25, 1.24, 1.23	-2.62, -4.98, -5.14, -5.27
1	11	24°C, DMAE	1.28, 1.27, 1.222, 1.218	-2.30, -2.48
1	12	24°C, DMAE	1.30, 1.28, 1.27, 1.24, 1.23	-2.73, -3.27
2	1 via 17	100°C, Zn(OAc) <sub>2</sub>	1.27, 1.26, 1.25, 1.22, 1.21	-
2	11	-18°C, DMF Zn(OAc) <sub>2</sub>	1.26, 1.20	-
2	12	-20°C, DMF Zn(OAc) <sub>2</sub>	1.26	-

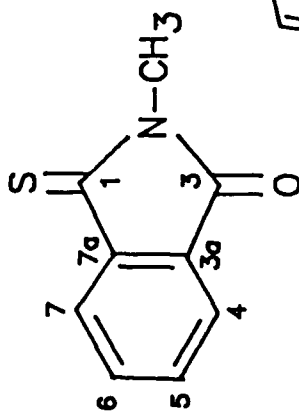
<sup>a</sup> N,N-dimethylaminoethanol



3

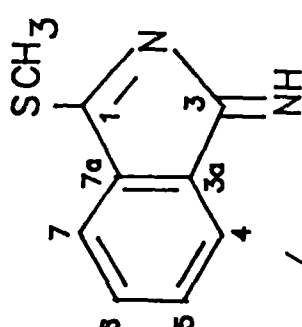


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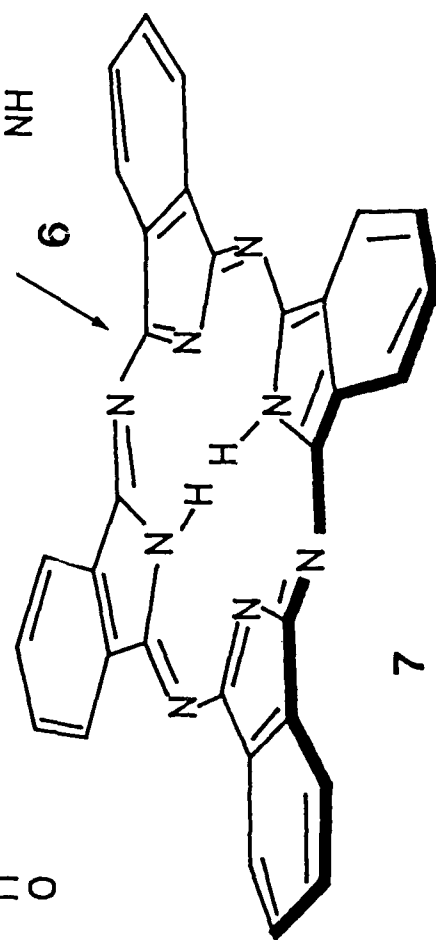


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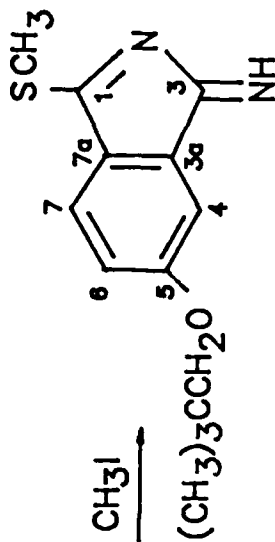
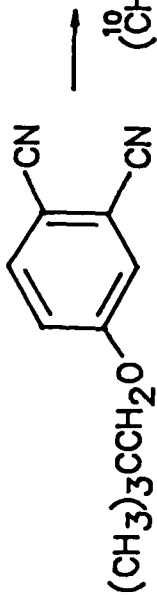
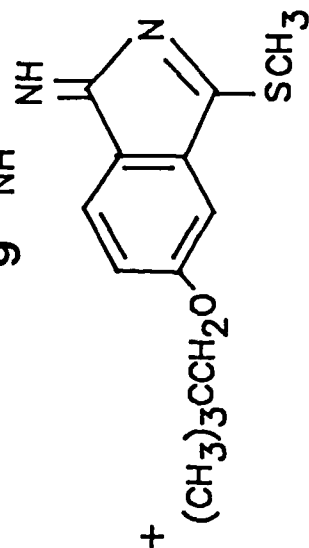
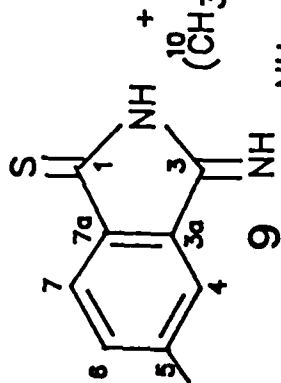
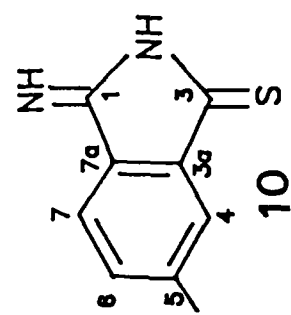


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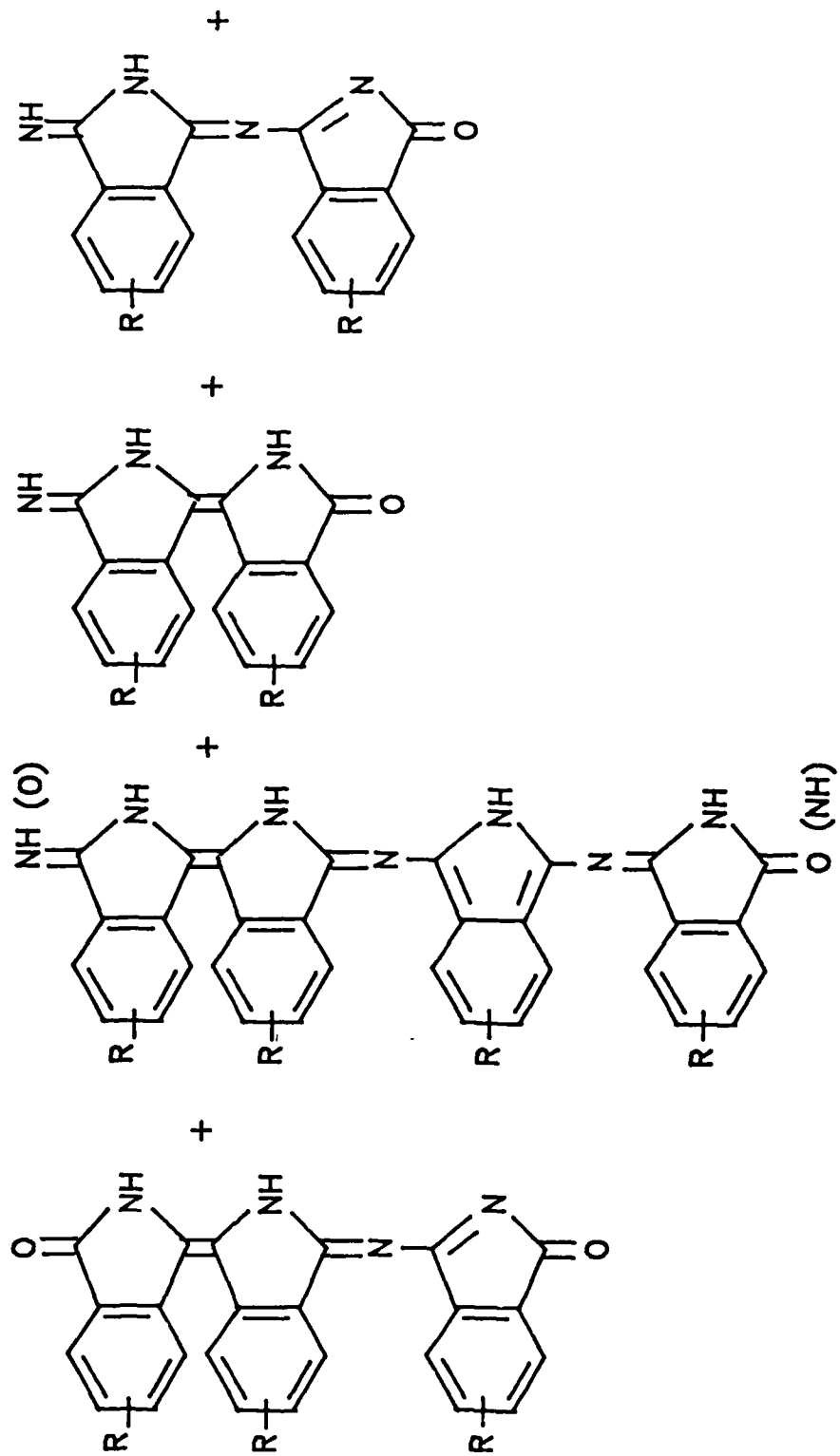
SCHEME I

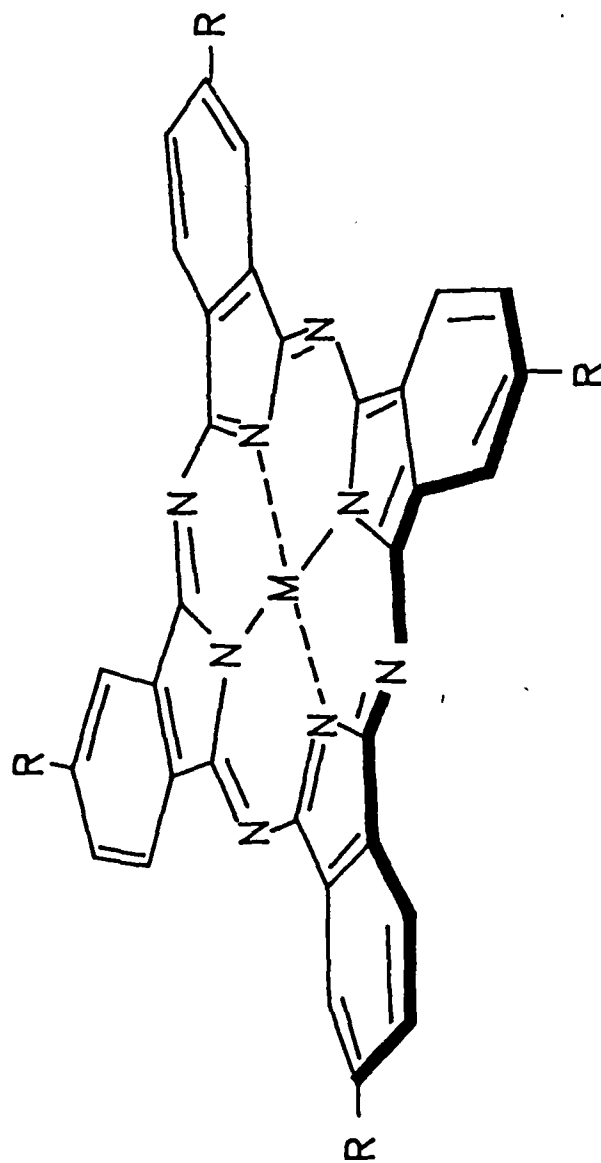


12

11

SCHEME II  
CONT'D ON  
NEXT PAGE





1  $R = OCH_2C(CH_3)_3$ ,  $M = H_2$

2  $R = OCH_2C(CH_3)_3$ ,  $M = Zn$

7  $R = H$ ,  $M = H_2$

SCHEME II

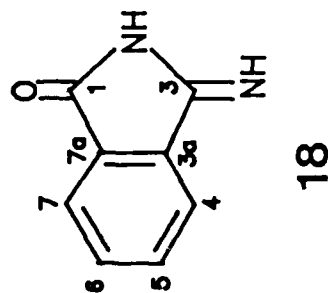
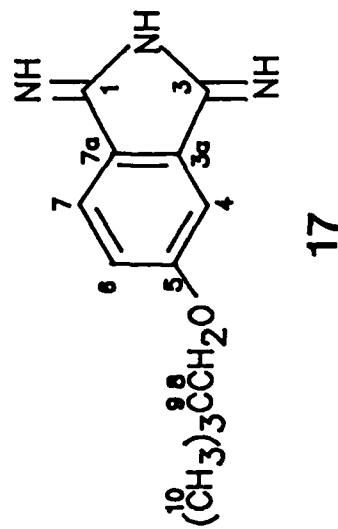


FIG.1. COMPOUNDS USED IN AIDING ASSIGNMENTS OF  $^{13}\text{C}$  NMR SPECTRA (TABLE 1)

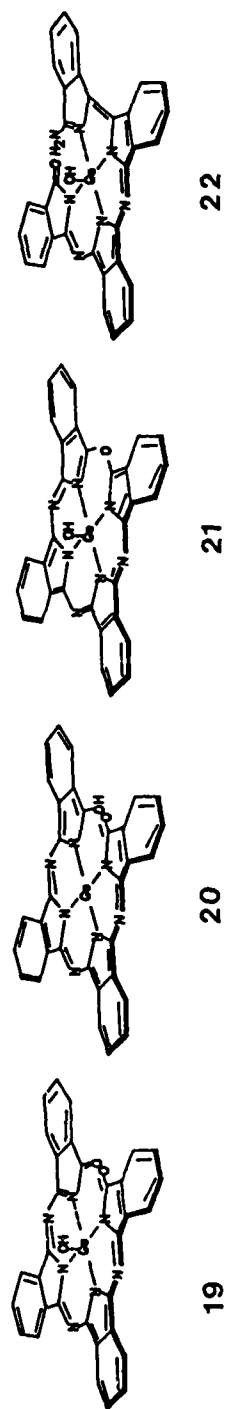


FIG. 2 REPORTED AND NEW SUGGESTED STRUCTURES FOR THE RED COMPOUND.